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(54) Blooming type, hard surface cleaning, and/or disinfecting compositions

(57) A blooming type, hard surface cleaning concentrate composition includes as a blooming system the following essential constituents: a cationic quaternary ammonium surfactant; an anionic carboxylated alcohol alkoxylate surfactant; a surfactant compatibilizing agent; and, water. Further optional constituents may also be included including additional anionic, cationic, nonionic, amphoteric and zwitterionic surfactants especially to provide a further deteritive effect; organic solvents such as alcohols, ethers, glycol ethers to aid in stain solubilization, as well as conventional additives such as coloring agents including dyes, fragrances, and others. In a preferred embodiment, the concentrate compositions and cleaning compositions also provide a germicidal effect to hard surfaces. The cleaning concentrates exhibit a characteristic bloom when admixed to a larger volume of water, yet are substantially clear and shelf stable as concentrate compositions.

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BLOOMING TYPE, HARD SURFACE CLEANING AND/OR DISINFECTING
COMPOSITIONS

5 The present invention relates to improvements in
cleaning compositions. More particularly, the present
invention is directed to improved hard surface cleaning
compositions and concentrates thereof, which feature
blooming when the concentrate is added to a larger
10 volume of water.

Cleaning compositions are commercially important
products and enjoy a wide field of utility in assisting
in the removal of dirt and grime from surfaces,
especially those characterized as useful with "hard
15 surfaces". One particular category of cleaning
compositions are those which are classed as pine oil
type cleaning compositions which typically contain a
significant amount, e.g., 5%wt. of naturally derived
and/or synthetically produce pine oils. Such
20 compositions generate a milky or cloudy appearance when
diluted with water in dilutions useful for cleaning
applications, and are generally provided as
concentrated composition which is subsequently diluted
with water by an end user/consumer to form a cleaning
25 composition therefrom. While such pine oil type
cleaning compositions are commercially significant and
in popular use, their use is not without attendant
shortcomings. For example, high levels of pine oil in
a cleaning composition are known to leave undesirable
30 surface residues, particularly on hard surfaces. This

effect may be minimized by the addition of further constituents, such as the use of certain surfactants which are useful in solubilizing and stabilizing the pine oil. However, such a solution raises further problems as many useful surfactants, and frequently the pine oil itself, are categorized as undesired volatile organic compounds ("VOC"). However, the removal of the pine oil itself is not desired nor in most case feasible as its presence is associated with the formation of the blooming effect when the concentrate is added to a larger volume of water. This blooming effect (also sometimes referred to as "break" in the United Kingdom and in other countries) is an important indicia for consumer acceptance for certain products, those which traditionally use pine oil to providing the blooming effect, as well as other products which do not contain pine oil but which nonetheless exhibit this very desirable blooming behaviour when added to a larger volume of water to form a cleaning and/or disinfecting composition therefrom.

Various formulations directed to the production of pine oil type cleaners with reduced pine oil content have been proposed. While advantageous, these compositions are not without attendant shortcomings, certain shortcomings which the present applicant addresses. Notwithstanding the present state of the art, there is yet a need for further improvements to blooming type hard surface cleaning compositions.

In accordance with the present invention, inventors have made the surprising discovery that

successful blooming type hard surface cleaners may be produced which do not include pine oil, but which nonetheless exhibits the much desired blooming behaviour which is associated with pine oil cleaners.

5 This surprising discovery now permits for the production of concentrate compositions which are transparent or relatively clear in appearance, but which when added to a greater volume of water such as to form a cleaning/disinfecting composition therefrom, exhibit the blooming behaviour which has hitherto been associated with pine oil containing compositions. This discovery permits for the production of cleaning and/or disinfecting compositions and concentrates thereof which contain no pine oil, yet which exhibit this

10 important identifying characteristics of pine oil type cleaning compositions. This discovery also permits for the production of aqueous cleaning and/or disinfecting compositions which exhibit blooming when added to a larger volume of water, but which may be selectively imparted with any of a number of different appearances and fragrances which is possible by the judicious selection of any of a number of dyes, fragrances, other colorants which may be added to the concentrate compositions to provide a desired color and a desired

15 scent.

20 In accordance with their discovery and in accordance with the present inventive teaching there are provided commercially acceptable shelf stable concentrated cleaning and/or disinfecting compositions

25 which exhibit blooming when their concentrated

cleaning compositions are diluted with a larger volume of water to form cleaning and/or disinfecting compositions. Such compositions contain no pine oil or pine oil fraction such as a terpineol fraction thereof, or which do not contain pine oil or pine oil fraction such as a terpineol fraction thereof in any significant amount, other than minor amounts such as might be used in a fragrance constituent, as the compositions do not rely upon pine oil or pine oil fractions to provide their blooming characteristic when diluted with water. In a further aspect of the invention, the present inventors provide processes for the formation for novel blooming type cleaning and/or disinfecting compositions. In a still further aspect of the invention there are provided processes for cleaning and/or disinfecting hard surfaces by applying effective amounts of a cleaning composition as taught in this specification to a hard surface in need of cleaning and/or disinfection.

The blooming type, aqueous hard surface cleaning and/or disinfecting compositions according to the invention comprise the following essential constituents which form the blooming system which is incorporated into the composition:

a cationic quaternary ammonium surfactant;
an anionic carboxylated alcohol alkoxylate surfactant;
a surfactant compatibilizing agent; and,
water.

The compositions according to the invention in many cases which comprise any of a number of further optional constituents which do not undesirably reduce or which diminish the operation of the blooming system described herein especially one or more further surfactants including anionic, cationic, nonionic, zwitterionic and/or amphoteric as well as mixtures thereof, one or more organic solvents such as lower alkyl alcohols, lower alkyl diols and glycol ethers, as well as one or more fragrances, coloring agents, chelating agents, germicidal compositions including those based on phenolic compounds, as well as other conventional additives.

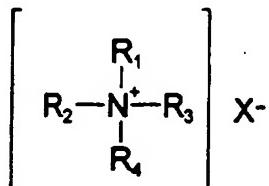
These inventive compositions still exhibit many of the desirable characteristics of pine oil type cleaning compositions described above, especially "blooming", but do not require the presence of pine oil to provide the blooming effect. Rather, selected known art dyes or other coloring agents, in conjunction with minor amounts of one or more fragrance materials especially those which provide a pine type scent may be included to the blooming system, as well as further optional surfactants and or organic solvents which are included to provide a deteritive property to the compositions. In this way, a cleaning composition which has the physical appearance and blooming characteristic of a conventional pine oil type cleaning composition may be provided without the presence of pine oil. Similarly, other blooming type cleaning and/or disinfecting compositions may be produced such as by including

different fragrances, i.e., those characteristic of lemon, various flora, in conjunction with a desired coloring additives, i.e., green, yellow, amber, red, etc. may be added as desired. In each case, a blooming type cleaning and/or disinfecting compositions may be produced. "Blooming" may be described as the change of the water's appearance from essentially colorless and transparent to that of a milky white or milky yellowish white, cloudy appearance. Concomitantly, in the concentrate compositions according to the invention, the lack of the overall amounts of pine oil typically found in prior art pine oil type cleaning concentrates, as well as the necessary compatibilizing agents required to solubilize the pine oil in such prior art cleaning concentrate provides the benefits of reduced volatile organic content of a concentrate or cleaning composition, as well as reduce the propensity of such compositions to form undesirable residues, especially pine oil residues upon cleaned surfaces.

The blooming system according to the invention includes at least one cationic quaternary ammonium surfactant; at least one anionic carboxylated alcohol alkoxylate surfactant; at least one surfactant compatibilizing agent which solubilizes the one cationic quaternary ammonium surfactant and the anionic carboxylated alcohol alkoxylate surfactant in a concentrate composition; and, water.

The at least one cationic quaternary ammonium surfactant according to the invention may be any of those which are known to the art, but preferably are

quaternary ammonium compounds and salts thereof include quaternary ammonium germicides which may be characterized by the general structural formula:

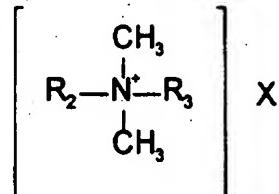


5 where at least one or R_1 , R_2 , R_3 and R_4 is a hydrophobic, aliphatic, aryl aliphatic or aliphatic aryl radical of from 6 to 26 carbon atoms, and the entire cation portion of the molecule has a molecular weight of at least 165. The hydrophobic radicals may
10 be long-chain alkyl, long-chain alkoxy aryl, long-chain alkyl aryl, halogen-substituted long-chain alkyl aryl, long-chain alkyl phenoxy alkyl, aryl alkyl, etc. The remaining radicals on the nitrogen atoms other than the hydrophobic radicals are substituents of a hydrocarbon
15 structure usually containing a total of no more than 12 carbon atoms. The radicals R_1 , R_2 , R_3 and R_4 may be straight chained or may be branched, but are preferably straight chained, and may include one or more amide or ether linkages. The radical X may be any salt-forming
20 anionic radical.

Exemplary quarternary ammonium salts within the above description include the alkyl ammonium halides such as cetyl trimethyl ammonium bromide, alkyl aryl ammonium halides such as octadecyl dimethyl benzyl ammonium bromide, N-alkyl pyridinium halides such as N-cetyl pyridinium bromide, and the like. Other suitable types of quarternary ammonium salts include those in which the molecule contains either amide or ether

linkages such as octyl phenoxy ethoxy ethyl dimethyl
benzyl ammonium chloride, N-
(laurylcocoaminoformylmethyl)-pyridinium chloride, and
the like. Other very effective types of quarternary
5 ammonium compounds which are useful as germicides
include those in which the hydrophobic radical is
characterized by a substituted aromatic nucleus as in
the case of lauryloxyphenyltrimethyl ammonium chloride,
cetylaminophenyltrimethyl ammonium methosulfate,
10 dodecylphenyltrimethyl ammonium methosulfate,
dodecylbenzyltrimethyl ammonium chloride, chlorinated
dodecylbenzyltrimethyl ammonium chloride, and the like.

Preferred quarternary ammonium compounds
which act as germicides and which are found useful
15 in the practice of the present invention include those
which have the structural formula:



wherein R₂ and R₃ are the same or different C₈-C₁₂alkyl,
20 or R₂ is C₁₂₋₁₆alkyl, C₈₋₁₈alkylethoxy,
C₈₋₁₈alkylphenoxy and R₃ is benzyl, and X is a
halide, for example chloride, bromide or iodide, or
methosulfate. The alkyl groups recited in R₂ and R₃,
may be straight chained or branched, but are preferably
25 substantially linear.

Such quartenary germicides are usually sold as
mixtures of two or more different quartenaries, such as
BARDAC® 205M, (presently commercially available from

Lonza, Inc., Fairlawn, NJ) which is believed to be a 50% aqueous solution containing 20% by weight of an alkyl dimethyl benzylammonium chloride (50% C14, 40% C16 alkyl); 15% by weight of an octyl decyl dimethylammonium chloride; 7.5% by weight of dioctyl dimethylammonium chloride; and 7.5% by weight of didecyl dimethylammonium chloride. A further useful 5
quaternary germicide is SYNCAL® 80% (presently commercially available from Hilton Davis Chemical Co., Cincinnati, OH) which is believed to comprise 80% by 10
weight of an alkyl dimethyl benzylammonium chloride (50% C14, 40% C12 and 10% C16 alkyl), 10% water and 10% ethanol. Further useful quaternary germicidal agents include BTC-8358®, an alkyl benzyl dimethyl ammonium 15
chloride (80% active) and BTC-818®, a dialkyl dimethyl ammonium chloride (both presently commercially 20
available from the Stepan Chemical Co., Chicago, IL). Additional suitable commercially available quaternary ammonium germicides of the alkyl dimethyl benzylammonium chloride type containing the same alkyl 25
dimethyl benzylammonium chloride mixture as that of SYNCAL® and which are generally referred to as quaternium salts include BARQUAT® MB-80, (presently commercially available from Lonza, Inc., Fairlawn, NJ) which is believed to be and 80% by weight solution (20% ethanol) of the quaternary, HYAMINE® 1622 believed to be an aqueous solution of benzethonium chloride, and HYAMINE® 3500, which is believed to be a 50% aqueous 30
solution of the quaternary (both presently commercially available from Lonza Inc., Fairlawn, NJ).

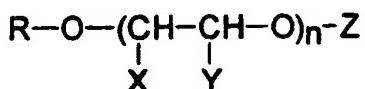
The cationic surfactant may be present in any amount which are found to exhibit the desirable characteristics of the invention, particularly that of a substantially clear to a relatively clear appearance in concentrated solution, as well as blooming when diluted with further water to form a cleaning composition. In preferred compositions, in addition to the blooming characteristics produced in conjunction with the anionic surfactant and the surfactant compatabilizing agent, the cationic surfactant also exhibits germicidal activity as is noted above.

Generally, this cationic surfactant is present in the concentrate compositions in amounts of 5% by weight and less, preferably in amounts of 0.1 - 4% by weight, but most preferably in amount of 1 - 2% by weight. It has been found by the inventors that the preferred amounts are in part dictated by toxicological considerations as an excess of the cationic component may pose an increasing risk of irritation to the eyes, skin and mucous tissues of a consumer. The preferred amounts are also in part dictated by economic considerations as an excess of the cationic component above these amounts generally requires a corresponding increase in the amount of the anionic component used in the blooming system formed herein.

The at least one anionic carboxylated alcohol alkoxylate surfactant according to the invention is an anionic surfactant which has been found to be effective in forming a water insoluble or poorly miscible complex when mixed with the quaternary ammonium compound

described above, which due to said insolubility or poor miscibility of the formed complex, renders an aqueous mixture containing the anionic carboxylated alcohol alkoxylate surfactant and the quaternary ammonium compound such an aqueous mixture turgid, milky or cloudy.

Particularly useful carboxylated alcohol alkoxylate compounds which are advantageously incorporated into the compositions of the invention include carboxylated alcohol alkoxylate surfactants according to the following general formula:



wherein R is a hydrophobic group, more preferably a C₆-C₁₈ alkyl group, n is a number in the range of 1 to 24, X and Y are independently selected from the group consisting of hydrogen, succinic acid radical, hydroxysuccinic acid radical, citric acid radical, and mixtures thereof, wherein at least one of X or Y is a succinic acid radical, hydroxysuccinic acid radical, or citric acid radical, and Z is H or -CH₂COOH. Certain anionic surfactants according to the immediately preceding general formula are presently commercially available as the Poly-Tergent® C series of anionic surfactants from the Olin Chem. Co., (Stamford, CT). Particularly preferred amongst these are the Poly-Tergent™ CS-1 composition which is believed to being a composition according to the formula above wherein R is a C₆-C₁₈ alkyl group, X and Y are independently H, CH₃, or the succinic acid

radical with at least one succinic acid radical being present, and where Z is H. Also useful is PolyTergent™ C9-62P a further carboxylated alcohol alkoxylate surfactant also available from the Olin Chemical Co

5 Other known anionic surfactants, while not particularly enumerated here may also find use in the present inventive compositions, as well as mixtures of one or more anionic surfactants.

10 The carboxylated alcohol alkoxylate is present in any amount which is found to exhibit the desirable characteristics of the invention, that of a relatively clear appearance in an aqueous solution when in the presence of an effective amount of the quaternary ammonium compound described above and further with an
15 effective amount of the surfactant compatibilizing agent described below, but that of blooming when diluted with further water to form a cleaning composition.

20 Generally, this anionic surface active agent is present in concentrate compositions in amounts of up to about 5% by weight, preferably in amounts of 0.1-5% by weight, but most preferably in amount of between 1 and 3.5% by weight.

25 Particular attention is to be paid to the relative proportions of the cationic surfactant to the anionic surfactant in the blooming system of the compositions according to the invention, as it is a feature of the invention that both the cationic quaternary ammonium surfactant and the anionic carboxylated alcohol alkoxylate surfactant, and surfactant compatibilizing agent be present in such amounts such that the
30

concentrate composition be relatively clear when present in the concentrate composition. Such a concentrate composition is relatively clear and is preferably transparent. However, upon the addition of
5 the said concentrate composition to a further amount of water, the solubility of these cationic surfactants and the anionic surfactants in the new larger volume of water is sufficiently reduced or disrupted which causes the newly formed composition to become turgid, or
10 cloudy and thus imitate the "blooming" behaviour of prior art pine oil cleaner type compositions. While not wishing to be bound by any theory, it is hypothesized that in the absence of a sufficient amount of the surfactant compatabilizing agent, the pendant carboxylic acid or carboxylic acid moieties of the
15 preferred species of anionic surfactants effectively complex with the quaternary ammonium in the quaternary ammonium compound and become insoluble or immiscible in an aqueous mixture, which then become visible due to the presence of the sufficiently long alkyl chain moieties which also constitute part of the preferred anionic surfactants. This effect may however be reversed by the addition of an additional,
20 sufficient amount of the surfactant compatibilizing agent to such a mixture, which addition solubilizes at least the anionic surfactant and/or the complexed cationic and anionic surfactants. Such solubilization effectively restores the clear appearance of the aqueous mixture containing the cationic and anionic
25 surfactants. It is contemplated that other anionic
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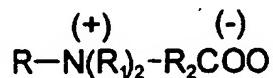
surface active agents having a first functional portion or group effective in forming a complex with the quaternary ammonium compound in water, and which has a second functional portion or group which is hydrophobic
5 in nature and which is insoluble or poorly miscible in water when such a complex is formed and in the absence of any further compatabilizing agent(s) become visible to the eye, may also be used.

The surfactant compatibilizing agent which
10 solubilizes the at least one cationic quaternary ammonium surfactant and the at least one anionic carboxylated alcohol alkoxylate surfactant may be any known art material which exhibits the properties described above. Such is believed to be determinable
15 by routine experimental techniques, such as by providing a volume of water having mixed therein amounts of the cationic quaternary ammonium surfactant compound and the anionic carboxylated alcohol alkoxylate surfactant compound which renders the volume
20 of water to be non-transparent, especially turgid or milky in appearance, and adding thereto an amount of a compound or composition which may be used to compatibilize the anionic and cationic surfactant compounds. Afterwards, an aliquot of this mixture may
25 then be added to a larger volume of water, such as a mixture:water dilution ratio of 1:64 at room temperature (approx. 20°C) to determine if such mixture evidences a blooming effect.

The inventors have found that one class of such
30 useful surfactant compatibilizing agents are water

soluble salts including, but not limited to monovalent alkali and/or polyvalent alkaline earth metal salts and ammonium salts. Non-limiting examples of such useful salts include: NaCl, MgCl₂, NaHCO₃, Na₂CO₃, NH₄Cl.

5 A further class of useful surfactant compatabilizing agents include certain amphoteric surfactants. Useful amphoteric surfactants include betaine compounds which exhibit the following general formula:



10 wherein R is a hydrophobic group selected from the group selected from alkyl groups containing from about 10 to about 22 carbon atoms, preferably from about 12 to about 18 carbon atoms, alkylaryl and arylalkyl groups containing a similar number of carbon atoms with a benzene ring being treated as equivalent to about 2 carbon atoms, and similar structures interrupted by amido or ether linkages; each R₁ is an alkyl group containing from 1 to about 3 carbon atoms; and R₂ is an alkylene group containing from 1 to about 6 carbon atoms.

15 Examples of preferred betaines include lauramidopropyl betaine, a commercial preparation of which is available under the tradename Mirataine® BB (from Rhône-Poulenc, Cherry Hill, NJ), and cocamidopropyl betaine available under the trade name Mackam™ DZ (from McIntyre Group Ltd., University Park, IL).

20 As noted previously, effective amounts of the surfactant compatabilizing agent may be any amount

which, when added to the aqueous concentrate mixture of at least one cationic quaternary ammonium surfactant and the at least one anionic carboxylated alcohol alkoxylate surfactant, but do not diminish the blooming characteristic of the concentrate composition when it is added to water. The present inventors have found that in the concentrate compositions according to the invention, such an effective amount may be a relatively small amount, and good compatibilizing behaviour has been observed with amounts of 10% by weight and less, with preferred amounts being 0.01 - 6% by weight of the compatabilizing agent. While amount less than 6% are to be preferred from an economic standpoint, it is to be understood that other amounts, including those greater than 6% by weight may be necessitated due to the selected cationic surfactant, and anionic surfactant, their relative amounts used, and their miscibility in water.

Water is added to concentrate compositions and in order to provide 100% by weight of the concentrate composition. The water may be tap water, but is preferably distilled and/or deionized water. If the water is tap water, it is preferably appropriately filtered in order to remove any undesirable impurities such as organics or inorganics, especially minerals salts which are present in hard water which may thus interfere with the operation of one or more constituents of the blooming system, as well as any other optional components of the liquid concentrates according to the invention. Water is added in amounts

which are sufficient to form the concentrated compositions which amount is sufficient to ensure the retention of a substantially clear characteristic when produced as a concentrate, but at the same time ensuring good blooming upon the addition of the concentrated composition to a further amount of water, or upon the addition of further water to the concentrate. Generally, water is present in the concentrate compositions in amounts in excess of about 5 50% by weight, preferably in amounts of in excess of 10 70% by weight, but most preferably in amount of between 80% to 92% by weight of the concentrate compositions according to the invention.

The compositions according to the invention in 15 many cases which comprise any of a number of further optional constituents which do not undesirably reduce or which diminish the operation of the blooming system described herein especially one or more further surfactants including anionic, cationic, nonionic, 20 zwitterionic and/or amphoteric as well as mixtures thereof, one or more organic solvents such as lower alkyl alcohols, lower alkyl diols and glycol ethers, as well as one or more fragrances, coloring agents, chelating agents, antioxidants, germicidal compositions 25 including those based on phenolic compounds, as well as other conventional additives. Such further optional constituents may be included in amounts found not to substantially interfere or detract from the blooming characteristics provided by the invention. Such 30 materials are known to the art, and are described in

5 *McCutcheon's Emulsifiers and Detergents (Vol. 1),*
 McCutcheon's Functional Materials (Vol. 2), North
 American Edition, 1991; Kirk-Othmer, Encyclopedia of
 Chemical Technology, 3rd Ed., Vol. 22, the contents of
which are herein incorporated by reference.

10 Known surfactants which provide a further
detersive effect to the concentrate compositions and
especially to the cleaning compositions formed
therefrom may be where such do not substantially
interfere or detract from the blooming characteristics
provided by the invention, and further desirably do
diminish the germicidal nature of the preferred cationic
quaternary ammonium compounds which are included in the
blooming system being taught herein. Such include
15 anionic, cationic, nonionic, zwitterionic and/or
amphoteric as well as mixtures thereof.

20 Useful anionic surfactants include the water-
soluble salts, particularly the alkali metal, ammonium
and alkylolammonium (e.g., monoethanolammonium or
triethanolammonium) salts, of organic sulfuric reaction
products having in their molecular structure an alkyl
group containing from about 10 to about 20 carbon atoms
and a sulfonic acid or sulfuric acid ester group.
(Included in the term "alkyl" is the alkyl portion of
25 aryl groups.) Examples of this group of synthetic
surfactants are the alkyl sulfates, especially those
obtained by sulfating the higher alcohols (C_8-C_{18} carbon
atoms) such as those produced by reducing the
glycerides of tallow or coconut oil; and the
30 alkylbenzene sulfonates in which the alkyl group

contains from about 9 to about 15 carbon atoms, in straight chain or branched chain. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 14.

Other anionic surfactants herein are the water soluble salts of: paraffin sulfonates containing from about 8 to about 24 (preferably about 12 to 18) carbon atoms; alkyl glyceryl ether sulfonates, especially those ethers of C₈₋₁₈ alcohols (e.g., those derived from tallow and coconut oil); alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 4 units of ethylene oxide per molecule and from about 8 to about 12 carbon atoms in the alkyl group; and alkyl ethylene oxide ether sulfates containing about 1 to about 4 units of ethylene oxide per molecule and from about 10 to about 20 carbon atoms in the alkyl group.

Other useful anionic surfactants herein include the water soluble salts of esters of α-sulfonated fatty acids containing from about 0 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and β-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Care should be exercised however in the selection of the anionic surfactants as it is known to the art that many anionic form insoluble complexes with cationic quaternary ammonium surfactants, and their use 5 in most cases is to be limited to minor amounts or wholly avoided.

Useful nonionic surfactants which may be included in the concentrate compositions include known art 10 nonionic surfactant compounds. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a water soluble nonionic surfactant compound. 15 Further, the length of the polyethenoxy hydrophobic and hydrophilic elements may various. Exemplary nonionic compounds include the polyoxyethylene ethers of alkyl aromatic hydroxy compounds, e.g., alkylated polyoxyethylene phenols, polyoxyethylene ethers of long 20 chain aliphatic alcohols, the polyoxyethylene ethers of hydrophobic propylene oxide polymers, and the higher alkyl amine oxides.

To be mentioned as particularly useful nonionic surfactants are alkoxylated linear primary and 25 secondary alcohols such as those commercially available under the tradenames PolyTergent® SL series (Olin Chemical Co., Stamford CT), Neodol® series (Shell Chemical Co., Houston TX); as alkoxylated alkyl phenols including those commercially available under the

tradename Triton® X series (Union Carbide Chem. Co., Danbury CT).

Known organic solvents which may be useful in providing a further cleaning benefit, especially in the loosening of stains may be added to the concentrate compositions of the invention. Such should be selected and be present in amounts which do not substantially interfere or detract from the blooming characteristics provided by the invention. Exemplary organic solvents include lower alkyl alcohols, lower alkyl diols and glycol ethers.

Lower alkyl alcohols which may be included are generally the water soluble C₁-C₈ alcohols as well as the water miscible C₁-C₈ diols examples of which include methanol, ethanol, propanol, isopropanol, butanol including t-butanol.

Exemplary glycol ethers water miscible glycol ethers including those having the general structure R_a-O-R_b-OH, wherein R_a is an alkoxy of 1 to 20 carbon atoms, or aryloxy of at least 6 carbon atoms, and R_b is an ether condensate of propylene glycol and/or ethylene glycol having from one to ten glycol monomer units. Preferred are glycol ethers having one to five glycol monomer units. These are C₃-C₂₀ glycol ethers.

Examples of more preferred solvents include propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, propylene glycol isobutyl ether, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol butyl ether, diethylene glycol phenyl ether, propylene glycol phenol

ether, and mixtures thereof. Further useful as the organic solvent are water-miscible ethers such as. diethylene glycol diethylether, diethylene glycol dimethylether, propylent glycol dimethylether, as well as lower esters of monoalkylethers of ethyleneglycol or propylene glycol such as. propylene glycol monomethyl ether acetate. Such are commercially available from Union Carbide, Dow Chemicals or Hoescht. Mixtures of organic solvents can also be used.

An optional, but sometimes desirable composition which may be added to the concentrate composition according to the invention is pine oil. Pine oil is a complex blend of oils, alcohols, acids, esters, aldehydes and other organic compounds, and is sometimes used as a solvent for certain types of stains. An important constituent of pine oil are terpene alcohols, especially alpha-terpineol. When included, the pine oil generally comprises at least about 60% terpene alcohols, especially alpha-terpineol. Particularly effective presently commercially available pine oils Glidco® Pine Oil™ 60 (available from Glidco Organics Corp., Jacksonville, FL, believed to contain approximately 60% terpene alcohols), Glidco® Pine Oil 60 (available from Glidco Organics Corp., Jacksonville, FL, believed to contain approximately 60% terpene alcohols); Glidco® Pine Oil 140 (available from Glidco Organics Corp., Jacksonville, FL, believed to contain approximately 70% terpene alcohols); Glidco® Pine Oil 80 (available from Glidco Organics Corp., Jacksonville, FL, believed to contain approximately 80% terpene

alcohols) Glidco® Pine Oil 150 (available from Glidco Organics Corp., Jacksonville, FL, believed to contain approximately 85% terpene alcohols); Glidco® Terpene SW (available from Glidco Organics Corp., Jacksonville, FL, believed to contain approximately 75% terpene alcohols); as well as Glidco® Terpineol 350 (available from Glidco Organics Corp., Jacksonville, FL, believed to contain approximately 100% terpene alcohols). Other products which can contain up to 100% pure alpha-terpineol, may also be used in the present invention.

When included, the pine oil constituent need be present in only minor amounts as they are not required to produce the blooming characteristics of the inventive compositions. Generally, they are present in reduced amounts in the concentrate compositions, i.e., in amounts of up to about 3% by weight, and if present are preferably included in amounts of from 0.01 - 2.5% by weight, but most preferably in amount of between 0.75-1.5% pine oil by weight. As with all of the weight percentages of the constituents described, the weight percentages are indicative of the weight percentages of the actives in a constituent containing preparation.

A further optional, but in some cases advantageous organic solvent which may be included are one or more terpene solvents, especially monocyclic monoterpenes and bicyclic terpenes which include terpinene, terpinolenes, limonenes, pinenes and mixtures thereof. Some may be found in fractions of pine oils noted above, but preferred are those which may be obtained

from the essence of citrus fruits of various types including from oranges, lemons and grapefruit. These are generally mixtures which include one or more of the following: d-limonene, dipentene, alpha-pentene, beta-pinene of which d-limonene is most preferred and may for example be obtained by distilling orange rind oil. Such a material is readily commercially available, has a very pleasant citrus fragrance, is known to have favorable cleaning properties and is derived from a naturally occurring material. If present such materials, especially materials which comprise 90%wt. and greater of d-limonene, need be present in only minor amounts, i.e., about 5%wt. and less, and generally about 3%wt. and less of the concentrate composition.

Certain of the optional constituents, such as the derivatives of citrus fruit may be provided with, or benefit from the addition of minor amounts of a stabilizer such as an antioxidant material, such as butylated hydroxytoluene.

Certain of the optional constituent, such as pine oil if included, may require a solubilizing adjuvant such as certain nonionic alkoxylated linear alcohol surfactants which aid in the dissolution of the pine oil in the water of the concentrate composition. Such useful nonionic alkoxylated linear alcohol nonionic surfactants are known, and may be commercially obtained from the Olin Chemical Co., (Stamford, CT) under the product line name of "Poly-Tergent®". Particular members of this product line which have been found

useful include; Poly-Tergent® SL-42 and Poly-Tergent® SL-62. Further useful nonionic surfactants include alkoxylated linear secondary alcohols, as well as alkoxylated alkylphenolic nonionic surfactants. Such 5 nonionic surfactants also provide a deteritive effect to the compositions.

Further exemplary pine oil solubilizing agents include C₁-C₈ alcohols, especially C₁-C₃ alcohols, of which isopropanol is preferred. An advantage of such 10 alcohols is in providing a further overall cleaning, i.e., stain solubilizing effect to the compositions.

It has generally been found that due to the relatively small amounts of the pine oil which are contemplated as optional constituents in the inventive 15 compositions would generally require a concomitantly small amount of the pine oil solubilizing agent, i.e., solubilizing adjuvant. Pine oil solubilizing agent in amounts of 15% by weight and less have been found to be effective to solubilize the pine oil, as well as optionally solubilizing other constituents which may be present in the concentrate compositions of the invention. Preferably, if present, such a pine oil 20 solubilizing agent in amounts of 15% and less by weight, preferably 0.01-10% by weight, and most preferably 0.1-5% by weight are used in the concentrate compositions.

Further optional, but desirable constituent include fragrances, natural or synthetically produced containing synthetic fragrance compositions, especially 30 those which are intended to mimic the scent of one or

more resins or oils derived from coniferous species of trees, viz., a scent characteristic of pine oil type cleaning concentrates as well as scents characteristic of other forms of flora, such as flowers. Other
5 desired fragrance materials may also be included in the compositions, and such are generally included in minor amounts, i.e., less than about 5%wt. of a concentrate compositions and care should be exercised so as not to undesirably inhibit the operation of the blooming
10 system according to the invention and as described above. Many organic materials which providing a fragrancing effect may be used and these per se, are known to the art. Such fragrances may be added in any conventional manner, admixing to a concentrate
15 composition or blending with other constituents used to form a concentrate composition, in amounts which are found to be useful to enhance or impart the desired scent characteristic to the concentrate composition, and/or to cleaning compositions formed therefrom.
20 Further optional, but advantageously included constituents are one or more coloring agents which find use in modifying the appearance of the concentrate compositions and enhance their appearance from the perspective of a consumer or other end user. Known
25 coloring agents, may be incorporated in the compositions in effective amount to improve or impart to concentrate compositions an appearance characteristic of a pine oil type concentrate composition, such as a color ranging from colorless to
30 a deep amber, deep amber yellow or deep amber reddish.

color. Other coloring agents, such as those which may impart a yellow color, such as may be associated with a lemon colored cleaning composition, or other colors may also be included. Such a coloring agent or coloring agents may be added in any useful amount in a conventional fashion, i.e., admixing to a concentrate composition or blending with other constituents used to form a concentrate composition.

Still further conventional additives which may be included are one or more hydrotopes such as sodium toluene sulfonate and sodium cumene sulfonate; one or more antibacterial agents such as orthobenzyl-para-chlorophenol although in preferred embodiments wherein the cationic quaternary ammonium compound has germicidal activity a further antibacterial agent is not normally required, detergent builder compositions, chelating agent especially useful as hard water ion sequestrants, as well as others. Each of such materials is generally only included in very minor amounts, i.e., each generally not exceeding 0.15%wt of the concentrate composition, but desirably even less.

Generally the total weight of such further conventional additives may comprise up to 30% by weight of a concentrated composition formulation.

What is to be understood by the term "concentrate" and "concentrate composition" in this specification and claims is the pre-consumer dilution and composition of the cleaning composition which is the essentially the form of the product prepared for sale to the consumer or other end user. Such a consumer or other end user

would then normally be expected to dilute the same with water to form a cleaning composition. It is to be understood however that nothing in this invention would bar its use as cleaning composition without any further dilution and it may be used in the concentrations in which it was prepared for sale. Similarly, what is to be understood by the term "cleaning compositions" are the water diluted compositions which are expected to be prepared by the consumer or other end user by mixing a measured amount of the "concentrate" with water in order to form an appropriately diluted cleaning composition which is suitable for use in cleaning applications, especially in the cleaning of hard surfaces.

As generally denoted above, the formulations according to the invention include both cleaning compositions and concentrates as outlined above which differ only in the relative proportion of water to that of the other constituents forming such formulations.

While the concentrated form of the cleaning compositions find use in their original form, they are more frequently used in the formation of a cleaning composition therefrom. Such may be easily prepared by diluting measured amounts of the concentrate

compositions in water by the consumer or other end user in certain weight ratios of concentrate:water, and optionally, agitating the same to ensure even distribution of the concentrate in the water. As noted, the concentrate may be used without dilution, i.e., in concentrate:water concentrations of 1:0, to extremely

dilute dilutions such as 1:10,000. Desirably, the concentrate is diluted in the range of 1:0.1 - 1:1000, preferably in the range of 1:1 - 1:500 but most preferably in the range of 1:10 - 1:100. The actual
5 dilution selected is in part determinable by the degree and amount of dirt and grime to be removed from a surface(s), the amount of mechanical force imparted to remove the same, as well as the observed efficacy of a particular dilution. Generally better results and
10 faster removal is to be expected at lower relative dilutions of the concentrate in water.

Example Formulations:

Preparation of Example Formulations:

Exemplary formulations according to the instant
15 invention were prepared in accordance with the following general procedure.

Into a suitably sized vessel, the following constituents were added in the sequence: water, cationic and anionic surfactant compositions of the
20 blooming system, the surfactant compatibilizing agent, and then any remaining constituents. All of the constituents were supplied at room temperature, and mixing of the constituents was achieved by the use of a magnetic stirrer. These constituents were used "as is" as supplied from their respective supplier. Mixing,
25 which generally lasted from 1 minute to 5 minutes, was maintained until the particular exemplary formulation attained uniform color and uniform clarity. The exemplary compositions were readily pourable, and

retained well mixed characteristics indicative of stability.

The exact compositions of the example formulations are listed on Table 1, below.

TABLE 1: EXAMPLE FORMULATIONS			
	Example Formulation: (in % weight)		
Constituent:	Ex.1	Ex.2	Ex.3
PolyTergent® CS-1	3.0	6.0	--
PolyTergent® C9-62P	--	--	4.0
BTC-8358	3.0	--	--
BTC-818	--	6.0	4.2
sodium chloride	2.0	--	--
Mackam® DZ	--	5.6	11.4
PolyTergent® SL-42	--	1.25	--
deionized water	to 100	to 100	to 100

5 PolyTergent® CS-1 is a polycarboxylated alcohol alkoxylate (50% active) available from Olin Chemical Corp.

10 PolyTergent® C9-62P is a polycarboxylated alcohol alkoxylate (50% active) available from Olin Chemical Corp.

BTC-835 is an alkyl benzyl dimethyl ammonium chloride (53% active) available from Stepan Chemical Co.

BTC-818 is a dialkyl dimethyl ammonium chloride (50% active) available from Stepan Chemical Co.

Mackram® DZ is cocoamidopropyl betaine (30% active) available from McIntyre Group Ltd.

Poly-Tergent® SL-42 is a nonionic alcohol alkoxylate available from Olin Chemical Corp.

Evaluation of Example Formulations:

5 Each of the example formulations was used to prepare an aqueous diluted form therefrom, of a concentration and dilution typical of conventionally used cleaning compositions useful in commercial/residential locations. These aqueous
10 dilutions were simply prepared by pouring one part by weight of each example formulation of Table 1 into 63 parts by weight of tap water (1:64 by weight dilution) at 20°C and at 40°C.

15 In each case, the addition of an example formulation to the water was accompanied by a change in the appearance of the water from transparent to a translucent cloudy, whitish appearance.

20 These aqueous dilutions were prepared to evaluate the degree of light transmittance, a measure of the opacity as well as of the blooming of each of the aqueous dilutions. Certain of these aqueous dilutions were also evaluated to determine the antimicrobial efficacy of the aqueous dilution. The results of the light transmittance evaluation was determined as a percentage of light transmitted through a sample of a particular aqueous dilution wherein the transmission of a like sample of water is assigned a percentage of 100%. Testing was performed by mixing a 5g aliquot of a particular example formulation with 315 g of tap water
25 (with approx. 100 ppm hardness), after which the sample
30

was mixed for 60 seconds and a transmittance reading at 620 nm wavelength was taken using a Brinkman model PC801 dipping probe colorimeter, which was set at 620 nm to determine the light transmission of each of the samples. Samples of each formulation at 20°C and at 40°C were evaluated, as well as the reference (pure tap water) sample used to calibrate the colorimeter to the reference 100% light transmission sample outlined above. The resulting determined values, reported as "Blooming" in Table 2 below provide an empirical evaluation, reported in percent transmittance ("%") of the degree of transparency of a diluted example formulation wherein 0% indicates complete opacity and 100% the transparency of a water sample as noted above. Accordingly, those results indicative of lower transmittance values identify samples exhibiting desirable turgid or cloudy appearances.

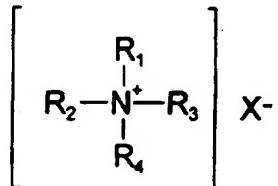
TABLE 2: TEST RESULTS OF TABLE 1 FORMULATIONS

Blooming	
Dilution of Example <u>Formulati</u> on:	transmission at 20°C
Ex.1	9.2 %
Ex.2	9.7 %
Ex.3	19.7 %

As can be seen from the results reported above,
the exemplary formulations featured good blooming
behaviour as cleaning composition, but were
substantially clear in the form of concentrate
compositions.

Claims:

1. An aqueous blooming type, hard surface cleaning composition concentrate which comprises a blooming system which includes the following essential constituents:
 - a cationic quaternary ammonium surfactant;
 - an anionic carboxylated alcohol alkoxylate surfactant;
 - a surfactant compatibilizing agent; and,
 - water.
2. The composition according to claim 1 wherein the cationic quaternary ammonium surfactant exhibits germicidal activity.
3. The composition according to claim 2 wherein:
 - the cationic quarternary ammonium compound is one according to the structure:



wherein;

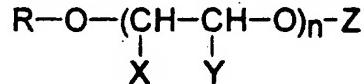
at least one or R_1 , R_2 , R_3 and R_4 is selected from hydrophobic, aliphatic, aryl aliphatic or aliphatic aryl radical of from 6 to 26 carbon atoms, and any remaining R_1 , R_2 , R_3 and R_4 are hydrocarbons of from 1 to 12 carbon atoms, wherein

any of R₁, R₂, R₃ and R₄ may be linear or branched and may include one or more ether or amide linkages; and,

X is a salt-forming anionic radical.

5

4. The composition according to claim 1 wherein:
the anionic surface active agent is capable of
forming a water insoluble or poorly water miscible
complex with the quaternary ammonium compound
which complex is miscible or soluble in water in
the further presence of a solubilizing effective
amount of the surfactant compatibilizing agent.
- 10
5. The composition according to claim 1 wherein:
the carboxylated alcohol alkoxylate surfactant
compound is one according to the following general
formula:
- 15



wherein: R is a hydrophobic C₆-C₁₈ alkyl group,
20 n is 1 - 24,
X and Y are independently selected from
the group consisting of hydrogen, succinic
acid radical, hydroxy succinic acid radical,
citric acid radical, and mixtures thereof,
25 wherein at least X or Y is a succinic acid
radical, hydroxy succinic acid radical,
citric acid radical or radical, and
Z is H or -CH₂COOH.

6. The composition according to claim 1 wherein:
the surfactant compatibilizing agent is selected
from water soluble salts and amphoteric betaine
compounds.
- 5
7. An aqueous cleaning compositions comprising the
aqueous blooming type, hard surface cleaning
composition concentrate according to claim 1
dispersed in water in a weight ratio of
concentrate:water from 1:0.1 to 1:1000.
- 10
8. A composition according to claim 1 substantially
as described according to the Examples.



The
Patent
Office

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Application No: GB 9616337.3
Claims searched: 1 to 8

Examiner: Michael Conlon
Date of search: 13 November 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.O): C5D (DHX, DHZ, DJX), A5E (EF, ET)

Int Cl (Ed.6): C11D

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	EP0363855 A1 (Hoechst) claim 4	1

- X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
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